

Modeling a Dry Etch Process for Large-Area Devices

R. J. Buss, D. S. Ruby, G. A. Hebner and P. Yang

Sandia National Laboratories, Albuquerque, NM 87185-0367 USA

Tel: 505 844-3504, Fax: 505 844-4816, email: rjbuss@sandia.gov

INTRODUCTION

There has been considerable interest in developing dry processes which can effectively replace wet processing in the manufacture of large area photovoltaic devices. Environmental and health issues are a major driver for this activity because wet processes generally increase worker exposure to toxic and hazardous chemicals and generate large volumes of liquid hazardous waste. Our work has been directed toward improving the performance of screen-printed solar cells while using plasma processing to reduce hazardous chemical usage [1].

The self-aligned selective-emitter (SASE) plasma-etchback and passivation process incorporates a sequence of three plasma treatments. Cells which have received standard processing through the printing and firing of gridlines undergo reactive ion etch (RIE) with an SF₆ plasma to etch away the most heavily doped part of the emitters. This is followed by a plasma deposition of silicon nitride and an ammonia plasma passivation step.

We have been developing plasma models to simulate each of these processes in sufficient detail that they can be used for process development and control. Reported here is the modeling of the SF₆ RIE plasma. In order to refine the chemical mechanism, a variety of diagnostic measurements were performed on the SF₆ plasma, including determination of silicon etch rates, mass spectrometry probes, Langmuir probe measurements of ion saturation currents, and gas temperature with a fluoroptic probe.

DESCRIPTION OF THE CALCULATIONS

The plasma simulations were done using the computer code AURORA [2], which employs CHEMKIN [3] and predicts the steady-state properties of a reactor for plasma-chemistry systems. Our approach to plasma modeling is to incorporate all the known chemistry and physics, and make best estimates of the unmeasured, but expected chemistry. For example, much of the plasma behavior is governed by electron collisions with SF₆. We rely heavily on cross section measurements [4,5,6] for the many channels such as ionization to give SF₅⁺, SF₄⁺ etc., fragmentation to give SF₅, SF₄, etc., attachment to give SF₆⁻, and vibrational and electronic excitation of the SF₆. The cross sections (σ) are measured vs. electron energy, and the predicted rate of a given reaction is calculated as the overlap of the electron energy distribution and the σ vs E curve. We convert the reported σ data into Arrhenius form for computational ease. This introduces a small error which is deemed negligible relative to uncertainty in the actual electron energy distribution in the plasma.

Reaction rates for the neutral reactions are very poorly known. Fortunately, the low densities of radicals in the plasma, and low total pressure result in relatively minor contribution from many of the expected radical-radical reactions. Three-body recombination reactions such as F + F + M = F₂ + M are expected to play a role even at these reduced pressures. The 3-body rates which have been reported are typically not

obtained using SF_6 as M. Therefore, it is necessary to estimate the 3-body rates for the many potential 3-body reactions and these rates are adjusted for best fit.

The importance of fluorine-based plasmas for etching silicon has led to some good fundamental work on the surface reactions of F atom on silicon. Our surface mechanism proposes a predominant reaction of F atoms with surface silicon to give SiF_2 groups and then further reaction to eliminate SiF_4 gas similar to the treatment of Flamm [7]. Ion assisted etch is included explicitly by allowing each positive ion to remove SiF_4 . The calculation distinguishes reaction at the chamber walls from silicon and uses a F atom wall recombination rate based on that estimated by Ganguli et al [8] but adjusted for best fit.

Our model incorporates 27 gas phase species including neutrals, electrons, positive and negative ions and a reaction mechanism with 138 gas-phase and 26 surface reactions.

EXPERIMENTAL

Etching of photovoltaic cells, and most diagnostics are done on a PlasmaTherm 790 reactor which is a parallel-plate system operating at 13.56 MHz. The reactor was instrumented with a differentially pumped mass spectrometer which probes the plasma gas directly with minimum wall recombination. Mass spectra are obtained for a range of power and pressure conditions with and without a silicon wafer in place. A Langmuir probe is used to obtain ion saturation current for a range of plasma conditions. In order to determine the silicon etch rate, 100 mm patterned wafers are etched and measured with profilometry at five locations. No significant radial non-uniformity of etch rate is observed.

On a separate research reactor, also capacitively-coupled, parallel plate and 13.56 MHz, the gas temperature of the SF_6 plasma was measured by fluoroptic probe. The reactor geometry is adjusted in the model calculations to allow comparison with this data.

RESULTS

We have developed a plasma chemistry model which gives a reasonably good fit to the data sets. Figure 1 shows a comparison of the etch rate data measured to the calculated rates graphed vs. pressure for five plasma powers. The overall trends are reproduced quite well, with a peak in etch rate observed at high power and intermediate pressure. At low power, the etch rate falls rapidly with

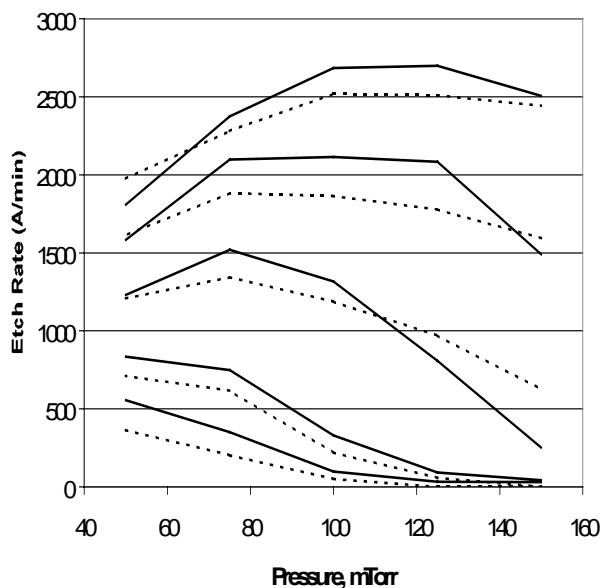


Fig. 1 Etch rate of silicon in SF_6 plasma. Experiment (solid lines) compared to model calculation (dashed lines). Curves are shown for powers (top to bottom) 100, 75, 50, 25, and 15 Watts.

increasing pressure. The model explains this falloff as due to electron capture by SF_6

depleting electrons so strongly, that the plasma is almost extinguished. In fact, at the highest pressures and low power, the calculation fails to converge.

The overall shape of the etch curves is predominantly the result of changes in the electron density, N_e , and temperature T_e . At high power and low pressure, N_e is highest but T_e is low. As pressure increases, N_e falls due to capture, and T_e increases as the rf power is coupled to fewer electrons. The increase in T_e leads to an increased production of F atoms from the reaction $e^- + \text{SF}_6$ which has a significant activation barrier. Eventually at high pressure, the loss of electrons to form negative ions dominates and F concentration falls. At low power, electron capture and negative ion formation tend to extinguish the plasma, with this phenomenon starting even at low pressure.

While overall trends in the etch data are determined by electron- SF_6 collisional phenomena, at high pressure and low power the calculation becomes sensitive to almost every reaction in the model. As N_e falls, small changes in any rate constant lead to major changes in N_e and T_e and hence the F atom density and etch rate. This effect probably will correspond to instability and difficulty in achieving reproducible etch rates. Small changes in wall cleanliness or temperature, for example, would be expected to influence etch rate. The model suggests that for manufacturing robustness, the plasma etch process should be operated in a parameter regime away from this metastable condition.

Figure 2 shows three graphs comparing plasma diagnostic measurements to the calculation. The agreement is not perfect, but the trends and magnitudes are reproduced quite well. Although the gas temperature measurements were obtained on a different

reactor with much smaller plasma volume, and hence higher power volume-density, the agreement is quite good. The break in the measured temperature above 40 watts is accompanied by a visual change in the plasma emission, and probably represents a reduced power density as the plasma volume increases.

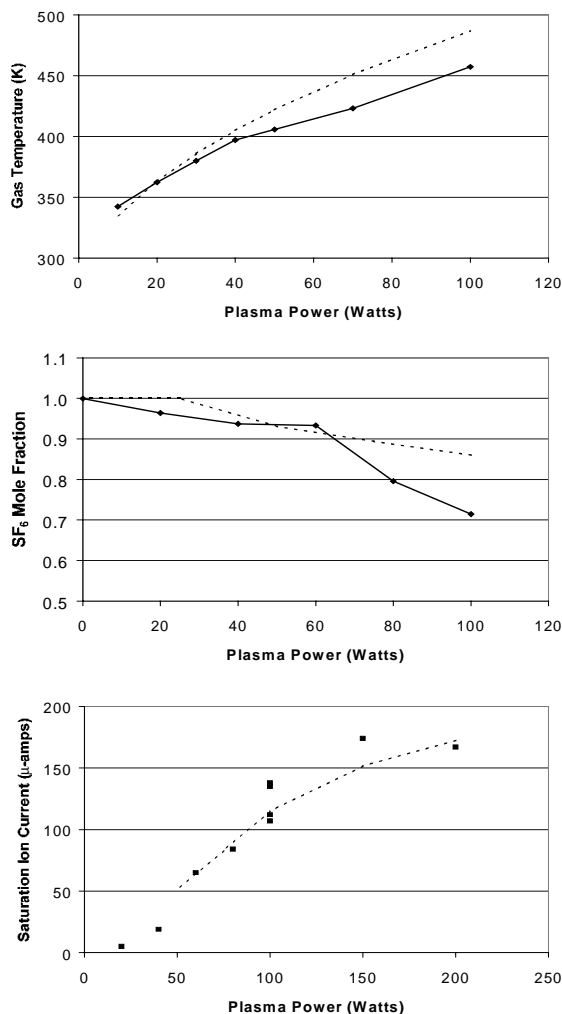


Figure 2. Comparison of calculation (dashed line) with experiment. Top: Fluoroptic probe measurement of gas temperature. Middle: Mass spectrometry measurement of SF_6 . Lower: Langmuir probe measurement of ion saturation current.

The comparison with mass spectrometer measurements of SF_6 mole fraction is the most

direct, because fragmentation patterns in the ionizer can be calibrated directly. Trends in other mass signals corresponding to the radicals SF₄ and SF₂ are used for fitting, but absolute densities of these species are less certain.

In order to compare the ion saturation current measurements, the calculated density of all 8 positive ions is used with the calculated T_e, and the Bohm velocities, v, for each ion, and the formula $I_{\text{sat}} = N_i * e * v$. Agreement with the measurements is quite good.

SUMMARY

We have studied a dry process for plasma-etchback of the emitter in full-size multicrystalline silicon cells. The plasma is pure SF₆ in a capacitively-coupled parallel plate commercial reactor. Plasma diagnostic measurements include etch rates, Langmuir probe measurements of ion saturation currents, mass spectrometric probes of the plasma gas and gas temperatures. A plasma model is developed and tested against these data. We obtain reasonable agreement with the measurements. From an analysis of the model results for the fall-off in etch rate at high pressure, we conclude that the plasma is likely to become very sensitive to minor system perturbations at high pressure and low power. Operation in this regime is liable to result in reduced process stability and reproducibility. Further refinement of the model will be possible as more kinetic data and diagnostic measurements become available, however the current model should be reliable enough to guide process scale-up and optimization

ACKNOWLEDGEMENTS

The authors would like to acknowledge many useful discussions with Dr. Pauline Ho on approaches to mechanism development, and Dr Ellen Meeks for initial work on the mechanism.

REFERENCES

1. D. S. Ruby, P. Yang, S. Zaidi, S. Brueck, M. Roy, and S. Narayanan, **Improved Performance of Self-aligned, Selective-Emitter Silicon Solar Cells**, Proc. of 2nd World Conf. on Photovoltaic Solar Energy Conversion, Vienna, July 1998.
2. E. Meeks, H. K. Moffat, J. F. Grcar, and R. J. Kee, **AURORA: A Fortran Program for Modeling Well Stirred Plasma and Thermal Reactors with Gas and Surface Reactions**, Sandia Report SAND96-8218, February 1996.
3. R. J. Kee, F. M. Rupley, J. A. Miller, M. E. Coltrin, J. F. Grcar, E. Meeks, H. K. Moffat, A. E. Lutz, G. Dixon-Lewis, M. D. Smooke, J. Warnatz, G. H. Evans, R. S. Larson, R. E. Mitchell, L. R. Petzold, W. C. Reynolds, M. Caracotsios, W. E. Stewart, and P. Glarborg, **Chemkin Collection, Ver. 3.02**, Reaction Design, Inc., (1997).
4. A. V. Phelps and R. J. Van Brunt, J. Appl. Phys. **64**(9), 4269 (1988).
5. D. Margreiter, G. Walder, H. Deutsch, H. U. Poll, C. Winkler, K. Stephan and T. D. Märk, Int. J. of Mass Spectr. and Ion Proc., **100**, 143 (1990).
6. M. Iio, M. Goto, H. Toyoda and H. Sugai, Contrib. Plasma Phys., **35**, 405 (1995).
7. D. L. Flamm, Pure & Appl. Chem., **62**(9), 1709 (1990).
8. P. S. Ganguli and M. Kaufman, Chem. Phys. Lett., **25**(2), 221 (1974).